The crystal structure of rare earth impurity centers R^{3+} in $Y_3Al_5O_{12}$: *Ab Initio* calculations

Cite as: AIP Conference Proceedings **1916**, 030005 (2017); https://doi.org/10.1063/1.5017438
Published Online: 11 December 2017

Vladimir A. Chernyshev, Alexander V. Serdcev, Vladislav P. Petrov, Anatoliy E. Nikiforov, Calin N. Avram, and Nicolae M. Avram

The Crystal Structure of Rare Earth Impurity Centers R^{3+} in $Y_3Al_5O_{12}$: *Ab Initio* Calculations

Vladimir A. Chernyshev[1], Alexander V. Serdcev[1], Vladislav P. Petrov[1], Anatoliy E. Nikiforov[1], Calin N. Avram[2] and Nicolae M. Avram[2, 3,a)]

[1]*Institute of Natural Sciences and Mathematics, Ural Federal University, Mira 19, 620002 Ekaterinburg, Russia*
[2]*Department of Physics, West University of Timisoara, V. Parvan 4, Timisoara 300223, Romania*
[3]*Academy of Romanian Scientists, Independentei Street 54, Bucharest 050094, Romania*

[a)]Corresponding author: nicolae.avram@e-uvt.ro

Abstract. In this paper we carried out the a*b initio* calculations of the impurity centers $Y_3Al_5O_{12}$: R^{3+} (R= La-Lu) by investigation doped crystal structure and its elastic properties. The crystal structure of impurity centers was investigated and the elastic constants of the crystals $RE_3Al_5O_{12}$ (RE = Y, La–Lu) were calculated. The effect of hydrostatic pressure on the elastic properties of $RE_3Al_5O_{12}$ (RE = Y, La–Lu) was investigated also. *Ab initio* calculations were performed in periodic CRYSTAL code within the framework of the MO LCAO approach by using hybrid DFT functionals. The results obtained can be used to interpret experimental data and predict the new properties of YAG: R^{3+} laser materials.

INTRODUCTION

Yttrium Aluminum Garnet (YAG, $Y_3Al_5O_{12}$) crystals activated by rare earth ions R^{3+} (R=La-Lu) is an active laser system, with applications spanning medical, industrial, military and scientific areas [1].$Y_3Al_5O_{12}$ attract also attention of researchers as promising materials for light-emitting diodes [2]. The crystal field on the impurity ion doped in such crystal is mainly determined by its closet surroundings-ligands and the ions following them. Information on the local crystal structure of impurity centers is necessary for studying the electronic spectrum, magnetic, elastic properties, etc. of impurity centers. YAG crystal belong to Ia3d (230 number group in International Table of Crystallography [3]) with eight molecular formula unit $Y_3Al_5O_{12}$ in the elementary cell [4]. Y^{+3} ions occupy dodecahedral sites and Al^{3+} ions are in octahedral and tetrahedral sites in the ratio of 2:3. This arrangement is the consequence of the differences in the ionic radii: O^{2-} (1.4 Å), Y^{3+} (1.281 Å), Al^{3+} (0.51 Å) [5]. Since the ionic radii of Y^{+3} ions and ions of rare-earth are relatively close trivalent ions of rare earth [5] the last can replace Y^{+3} ions by doping.

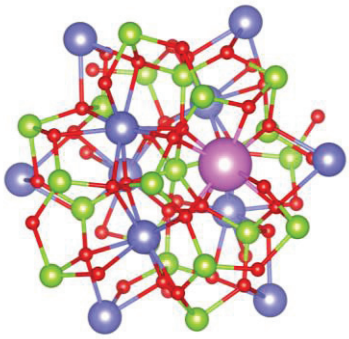

FIGURE1a). Impurity center

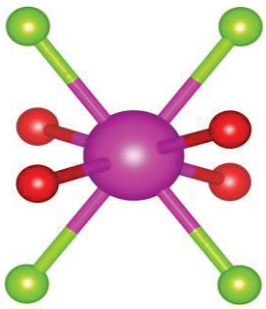

FIGURE1b). Rare ion and his ligands

TIM17 Physics Conference
AIP Conf. Proc. 1916, 030005-1–030005-5; https://doi.org/10.1063/1.5017438
Published by AIP Publishing. 978-0-7354-1608-6/$30.00

Figure 1a) presents the impurity center $Y_3Al_5O_{12}:R^{3+}$ and Figure 1b) presents impurity ion with its closet ligands. In these pictures red ions are oxygen, green-aluminum, blue-yttrium and R –lilac. According to [4] in Fig.1b) the R ion (purple) has as ligands 4 O^{2-} ions at distance ≈ 2.3 Å (red spheres) and 4 O^{2-} ions at distance ≈ 2.4 Å (green spheres). The aim of this paper is the investigation, from a theoretically point of view, the crystal structure of impurity centers, calculation the elastic constants of doped crystals and studying the effect of hydrostatic pressure on the elastic properties of the system$Y_3Al_5O_{12}:R^{3+}$.

METHODS OF CALCULATION

The calculations have been performed within the framework of the MO LCAO approach by using the periodic CRYSTAL14 code [6]. The best reproduction of the crystal structure and dynamics of the $Y_3Al_5O_{12}$ was provided by the DFT functional B3PW [7] which taken into account the direct Hartree-Fock exchange and gradient corrections.

A semi local quasi-relativistic pseudopotential ECP28MWB [8, 9], including the 3d shell, was used to model the electronic structure of yttrium, successfully applied in our previous work [10]. A valence basic set including diffuse and polarized d- and f-orbitals was used to describe the outer shells of yttrium.

A significant degree of covalence of the bonds required a careful choice of the Al and O bases. As calculations have shown, it is necessary to use a sufficiently complete basic set for describing Al to obtain an adequate description of the chemical bond and gap in the band structure.

Trial calculations were made with all Al and O bases sets available on the CRYSTAL 14 website. Based on the results of calculations, a basis set Al_s8511p511d11_Heifets_2013 [11] was chosen for modeling the electronic structure of aluminum. For oxygen, a basis set O_8-411_Towler_1994 [12] was chosen to modeling its electronic structure, along mentioned above, in order to the best describe the YAG structure. Results of the calculations are presented in Table 1.

TABLE 1. The results of calculating the physical properties of the YAG

	Experiment [13]	Calculation
Lattice constant, Å	12.003	12.008
Density ρ, g/cm^3	4.55	4.58
Bandgap, eV	8.0	7.18
C_{11}, GPa	333.0	353.1
C_{12}, GPa	111.0	109.7
C_{44}, GPa	115.0	123.4

In order to determine the degree of covalence of bonds in the YAG the map of charge density was made. The map indicates that the Y-O and Al-O bonds have ion-covalent character. The same conclusion is obtained from analysis of Mulliken population, from the calculations of the degrees of oxidation states of the ions (Tables 2) and from the results of calculations for charges on bonds (|e|): 0. 0185 (Y-O) and 0.0955 (Al-O).

TABLE 2. Charges of ions in the YAG, |e|

	Assuming an ionic bond	Calculation (according to Mulliken)
Y	+3	+2,030
Al	+3	+2,201
O	–2	–1,446

RESULTS AND DISCUSSIONS

Yttrium-aluminum garnet has a complex crystal structure, and therefore the supercell method was not used in the simulation. By modeling the defect, one of the yttrium ions in the unit cell was replaced by a lanthanide ion without changes of symmetry group of ideal YAG crystal. The results of the calculations for lattice constants of doped crystals $Y_3Al_5O_{12}:R^{3+}$ (R=La-Lu) the radii of first and second spheres of coordination are given in Table 3.

We should underline based on the data from Table 3 that for the impurity centers of R^{3+} in $Y_3Al_5O_{12}$, the distortion of the crystal lattice is localized within first two coordination spheres. The replacement of yttrium by the R^{3+} ion (R = La-Ho) leads to an expansion of 1-2 coordination spheres within 0.1 Å, which decreases from

lanthanum to holmium (the change in bond lengths with ligands is less than 5%). When yttrium is replaced by the isovalent erbium ion, the distortion is practically absent and in the case of the replacement of yttrium by the R^{3+} ion from the end of the R series (R = Tm-Lu), the calculations predict the compression of the first two coordination spheres in the range 0.02 Å, increasing from thulium to lutetium.

TABLE 3. The lattice constants and radii of the first two coordination spheres of $Y_3Al_5O_{12}:R^{3+}$ (R=La-Lu)

Ln ion	Lattice constant. Å		Radius of the coordination sphere. Å	
	Experiment [14,15]	Calculation	First sphere	Second sphere
La	-	12.411 2.417	2.417 2.404	2.594
Ce	-	12.362	2.575	2.575
Pr	-	12.317	2.558	2.558
Nd	-	12.273	2.542	2.542
Pm	-	12.224	2.523	2.523
Sm	-	12.205	2.515	2.515
Eu	-	12.174	2.503	2.503
Gd	12.111	12.143	2.491	2.491
Tb	12.074	12.110	2.479	2.479
Dy	12.038	12.079	2.467	2.467
Ho	12.015	12.049	2.456	2.456
Er	11.981	12.022	2.446	2.446
Tm	11.957	11.997	2.437	2.437
Yb	11.929	11.971	2.427	2.427
Lu	11.912	11.950	2.419	2.419

The modeling of the $RE_3Al_5O_{12}$ structures is also of practical interest, and we have calculated the elastic constants for some $RE_3Al_5O_{12}$ (RE = La, Nd, Gd, Er, Lu, Y) structures. From the calculated elastic constants for these structures the Cauchy relation and the anisotropy indices (Universal, Zener and Every) [16-19] were calculated as function of pressures for 0-10 GPa (Table 4) and they suggested a high isotropy of all investigated crystals.

TABLE 4. Elastic properties of $RE_3Al_5O_{12}$ (RE = Y, La, Nd, Gd, Er, Lu) crystals under hydrostatic pressure.

	P. GPa	YAG	LaAG	NdAG	GdAG	ErAG	LuAG
Universal anisotropy index A^u	0.0	0.000407	0.014890	0.004999	0.000429	0.000414	0.002857
	2.5	0.000396	0.023843	0.010619	0.002504	0.000000	0.001190
	5.0	0.000385	0.040516		0.004062	0.000391	0.000387
	7.5	0.001504			0.006747	0.000764	0.000000
	10.0	0.002572			0.009706	0.001867	0.000000
Zener anisotropy index A_Z	0.0	1.014314	0.894009	0.936174	0.981883	1.019924	1.048504
	2.5	0.995004	0.869130	0.910538	0.958452	1.000567	1.032282
	5.0	0.978326	0.832620		0.942119	0.986992	1.016080
	7.5	0.965807			0.927609	0.973238	1.005932
	10.0	0.954627			0.914458	0.961041	0.993479
Every anisotropy index A_E	0.0	−0.015170	0.107951	0.067930	0.018941	−0.020991	−0.051622
	2.5	0.005226	0.137539	0.100521	0.042753	−0.000589	−0.033987
	5.0	0.022389	0.201068		0.058829	0.013330	−0.017117
	7.5	0.034814			0.072846	0.027097	−0.006399
	10.0	0.045634			0.085467	0.039033	0.007096
Cauchy ratio. C_{11}/C_{44}	0.0	0.888646	0.959392	0.870921	0.911458	0.900290	0.884785
	2.5	0.911464	0.888431	0.758346	0.941205	0.925018	0.902769
	5.0	0.934695	0.597549		0.965799	0.951088	0.880762
	7.5	0.963042			0.986538	0.974546	0.855038
	10.0	0.988024			1.001914	0.996086	0.836898

As can be seen from Table 4, the A^u index for all structures $RE_3Al_5O_{12}$ (RE = La–Lu, Y) is small. In the absence of pressure, the universal anisotropy index for experimentally stable structures (RE = Gd–Lu, Y) is significantly smaller than for (RE = La, Nd). The higher A^u value for the LuAG structure rapidly decreases with pressure and becomes close to the value A^u for other stable structures (Table 4). We note the different behavior of the anisotropy index A^u for stable and unstable structures. In unstable structures, the anisotropy index increases with increasing pressure, so the structure becomes more anisotropic. While in stable structures it decreases with increasing pressure. For the "boundary" crystal GdAG, the growth of A^u with increasing pressure, but significantly slower than that of unstable LaAG–EuAG, appears. Zener's anisotropy index [16] increases from La to Lu, while it is close to unity (0.89-1.05). According to our calculations, Zener's index $A_Z > 1$ for compounds $RE_3Al_5O_{12}$ (RE = Er, Lu), which are stable in the structure of garnet. For the compounds $RE_3Al_5O_{12}$ (RE = La, Nd) which are unstable in this structure, the Zener index $A_Z < 1$. For the "boundary" GdAG, the calculation predicts $A_Z < 1$, but the absolute value of the deviation is small. According to calculations, the Zener index decreases with pressure for all crystals (Table 4).

The calculations also predict a different sign of Every anisotropy index [19] for stable (RE = Er, Lu) and unstable (RE = La, Nd) crystals in the garnet structure (Table 4, line “P = 0”). This index for the "boundary" GdAG is $A_E > 0$, but its absolute value is small. According to our calculations, with hydrostatic pressure, the index increases for all crystals

As the calculations show, the Cauchy relation for stable structures with pressure practically does not change or increases whereas for unstable structures, it decreases, moving away from unity.

CONCLUSIONS

The crystal structure of the impurity centers R^{3+} in $Y_3Al_5O_{12}$ investigated by *ab initio* level shown that the distortions of the crystal lattice are localized within first two coordination spheres around the impurity centers. The replacement of yttrium by the R^{3+} ion (R = La-Ho) leads to an expansion of 1-2 coordination spheres within 0.1 Å. In the case of the replacement of yttrium by the R^{3+} ion from the end of the R series (R = Tm-Lu), the calculations predict the compression of the first two coordination spheres in the range 0.02 Å, increasing from thulium to lutetium. When yttrium is replaced by the isovalent erbium ion, the distortion is practically absent.

Ab initio calculation of elastic constants and anisotropy indices of crystals $RE_3Al_5O_{12}$ (RE = La-Lu, Y) and the influence of hydrostatic pressure on these structures is presented. It is shown that the anisotropy indices (Universal, Zener and Every) have qualitatively different behavior for stable (RE = Gd-Lu) and unstable (RE = La, Nd) YAG structure compounds. The universal anisotropy index decreases with pressure in stable structures and increases for unstable structures, so that the crystal becomes more anisotropic.

The Cauchy relation for stable structures practically does not change or approaches unity by pressure, and for unstable structures it moves away from unity.

Zener index for all compounds $RE_3Al_5O_{12}$ (RE = La-Lu, Y) is close to unity, which indicates a high degree of elastic isotropy. The absolute values of the other anisotropy indices also indicate this. All these conclusions could be check and used in future applications.

ACKNOWLEDGMENTS

The authors V.A.C., V.P.P., A.E.N. gratefully acknowledge financial support from the Ministry of education and science of Russia under Project no. 3.9534.2017/BP, the Russian Foundation for Basic Research (Project no. 16-33-00437 vol a) and financial support by Act 211 Government of the Russian Federation, contract № 02.A03.21.00

REFERENCES

1. W. Koechner, *Solid state Laser Engineering* (3rd ed.), springer, Berlin Heidelberg, 1992. , *J. Chem. Soc,* **948** (1948).
2. S. Nishiura, A. Tanabe, K. Fujioka, and Y. Fujimoto, Opt. Mater. **33**, 688(2011).
3. T. Hahn Ed., *International tables for crystallography*, Vol. A, Springer, Berlin, 2005.
4. A. Speghini, F. Piccinelli, M. Bettinelli, Opt. Mater. **33**, 247 (2011).
5. R. D. Shannon, Acta Cryst. A**32**, 751(1976).

6. R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco, M. Llunell, M. Causa and Y. Noel, CRYSTAL14, (2014) *CRYSTAL14 User's Manual*. University of Torino, Torino.
7. A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
8. Energy Consistent Pseudopotentials of the Stuttgart, http://www.tc.uni-koeln.de/PP/clickpse.en.html.
9. D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta. **77**, 123 (1990).
10. V. A. Chernyshev, V. P. Petrov, A. E. Nikiforov, D. O. Zakir'yanov, AIP Conf. Proc., **1694**, 030004 (2015).
11. E. Heifets, E. A. Kotomin, A. A. Bagaturyants, J. Maier, J. Phys. Chem. Lett. **6,** 2847 (2015).
12. M. D. Towler, N. L. Allan, N. M. Harrison, V. R. Saunders, W. C. Mackrodt, E. Apra', Phys. Rev. B **50**, 5041 (1994).
13. E. G. Spencer, R. T. Denton, T. B. Bateman, W. B. Snow, L. G. Van Uitert, J. Appl. Phys. **34**, 3059 (1963).
14. C. B. Rubinstein and R. L. Barnes, Amer. Miner. **50**, 782 (1965).
15. R. D. Shannon, M. A. Subramanian, T. H. Allik, H. Kimura, M. R. Kokta, M. H. Randles, G. R. Rossman, J. Appl. Phys. **67**, 3798 (1990).
16. S. I. Ranganathan, M. Ostoja-Starzewski, Phys. Rev. Lett. **101**, 055504 (2008)
17. W. Voigt, *Lehrbuch der Kristallphysik*, Taubner, Leipzig, 1928.
18. A. Reuss, Z. Angew, Math. Mech. **9**, 49 (1929).
19. A. G. Every, Phys. Rev. B. **22,** 1746-1760 (1980).